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CANADIAN PATENT

CONTROL OF MELT INDEX OF LOW PRESSURE POLYOLEFINS VIA TELOMERIZATION WITH HYDROGEN

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No. OF CLAIMS 9 - No drawing

This invention relates to the polymerization of alpha-olefins. More particularly, the invention relates to an improved method for controlling the molecular weight of polyolefins in certain processes yielding polymers of high density (0.920 to 0.970).

Catalysts of the coordination type for the polymerization of olefins have become well known. One of the troublesome problems encountered in the development of processes based on such catalysts is the problem of controlling molecular weight of the product. In the absence of any control, these catalysts frequently produce polymer of a molecular weight so high, and a melt index so low, as to preclude the use of the polymer in many important practical applications, such as extrusion or molding applications. One method of controlling the melt index of polyolefins is the "solution process" of Anderson, Bruce, and Fallwell. In this process, described in U. S. Patent 2,862,917, issued December 2, 1958, the olefin is polymerized in the presence of a liquid hydrocarbon medium under conditions of temperature and pressure which maintain both the polymer and the monomer in solution. The solution process affords the advantage of relatively precise control of the molecular weight, and thus of the melt-flow characteristics of the product, by control of the reaction temperature within the range of 150° to 300°C.

To achieve a polymer having a higher melt index, and thus a lower molecular weight, it is necessary in the solution process to increase the reaction temperature. Unfortunately, high reaction temperatures are undesirable, since the efficiency of the coordination catalyst falls off rapidly with increasing temperature. Moreover, when

alpha-olefin copolymers, such as an ethylene-butene copolymer, are prepared in the solution process, it has been found that progressively smaller amounts of the higher olefin are present in the resultant copolymer as the reaction temperature is increased, thus offering further complications in the production of a given copolymer composition. On the other hand, the solution process is advantageous since it permits obtaining a product having a narrower molecular weight distribution, that is, a more uniform product. Hence, it would be desirable to provide new methods for controlling the molecular weight of polyolefins.

It is an object of this invention to provide a method for producing lower molecular weight polymers and copolymers of alpha-olefins, which involves the solution polymerization process at substantially reduced reaction temperatures. A further object is to provide a polymerization process for olefins in which improved catalytic efficiency of coordination catalysts is achieved. Other objects will appear hereinafter.

The objects of this invention are accomplished by a process which comprises polymerizing an alpha-olefin in a liquid hydrocarbon medium containing a catalyst formed by admixing from one to two compounds of the class consisting of titanium salts, vanadium salts, titanium alkoxides, and vanadium alkoxides with a compound having at least one metal-to-hydrocarbon bond, said polymerization being performed in the presence of less than 60 parts per million of hydrogen (based on the total reactor feed) at a temperature and pressure so chosen as to maintain both the olefin monomer and polymer dissolved in the hydrocarbon medium. Thus, the

combination of the solution process of polymerizing olefins and the presence of very small amounts of hydrogen provides improved control of the melt index of the products. For example, under certain conditions a temperature of about 250°C. is required in the absence of hydrogen to obtain a polyethylene of melt index 2.5. With only about 6 parts per million (by weight) of hydrogen in the reactor feed, polymer of the same melt index can be made at 200°C.

Suitable alpha-olefins for use in this invention are the olefins having one terminal $-CH=CH_2$ group and no other non-aromatic unsaturation and containing from 2 to about 10 carbon atoms per molecule. Such olefins include ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-heptene, etc. The hydrogen is preferably metered into the reactor along with the olefin or olefin mixture to be polymerized. As little as 2 parts per million of hydrogen, preferably from 4 to about 40 parts per million, by weight based on the total reactor feed produce the advantages of the present invention.

Generally, the minimum temperature for the polymerization will be above 100°C. Preferably, the minimum reaction temperature exceeds the melting point of the polymer to be produced in order to achieve the necessary solubility of the polymer in the inert solvent that is used. The reaction pressure should be sufficient to maintain the solvent in the liquid phase. Preferably, the pressure used will exceed the critical pressure of the alpha-olefin.

Catalysts of the coordination type are used in the process of this invention. The catalyst is, for example, composed of a titanium halide and a reducing component, such as lithium aluminum tetraalkyl. A preferred catalyst combina-

tion is vanadium oxychloride, titanium tetrachloride and aluminum triisoprenyl. The catalyst may be prepared prior to or during the reaction and is employed in an amount sufficient to produce the desired conversion of the olefin to polymer.

The inert solvent used as the reaction medium may be an aliphatic, aromatic, or cycloaliphatic hydrocarbon, such as heptane, toluene, and cyclohexane. The material chosen must be a solvent for the monomer and polymer produced in the reaction. Cyclohexane and pentane are the preferred reaction media. The amount of olefin or olefins in the system is generally maintained in excess of the solubility limit in the solvent. In the solution itself, the olefin is present in preferred amounts of about 10% to about 20% by weight, and the polymer is present generally in like amounts.

The invention is illustrated further by means of the following examples. In these examples, the equipment and procedure used are those of Example 1 of the Anderson et al. patent U.S. 2,862,917, except as noted below.

EXAMPLE I

With ethylene as monomer, cyclohexane as the solvent, titanium tetrachloride, vanadium oxychloride and aluminum trisobutyl as catalyst components, the following results were obtained under the conditions specified.

Run No.	1	2	3	4
Temperature, °C.	252	200	199	202
Pressure, atm.	135	135	135	135
Weight ratio solvent/monomer	9.8	9.0	7.9	10.1
Hydrogen concentration, ppm.	0	0	4.6	7.3
Conversion, % monomer	91.5	88.3	89.7	90.5
Melt index of polymer	3.1	0.20	0.9	2.52
Density of polymer	0.959	0.960	0.960	0.960

EXAMPLE II

With the materials specified in Example I, the following results demonstrate the advantages of the invention at temperatures lower than those normally used for the solution process.

Run No.	1	2
Temperature, °C.	132	132
Pressure, atm.	135	135
Weight ratio solvent/monomer	9.0	10.2
Hydrogen concentration, ppm.	0	58
Conversion, % monomer	88.0	89.7
Melt index of polymer	0.0005	2.35
Density of polymer	0.957	0.962

EXAMPLE III

With ethylene and 1-butene (23% butene based on total monomers) as comonomers and the other materials specified in Example I, the following results were obtained.

Run No.	1	2	3
Temperature, °C.	220	132	132
Pressure, atm.	135	135	135
Weight ratio solvent/monomers	9.0	9.0	10.4
Hydrogen concentration, ppm.	0	0	36
Conversion, % monomer	90.0	89.0	91.0
Melt index of polymer	2.5	0.005	2.6
Density of polymer	0.930	0.928	0.930

The results show that the process of this invention affords a substantial reduction in the molecular weight of the polymer, thereby permitting the achievement of any desired degree of polymerization or melt index with the use of a much lower reaction temperature than was possible heretofore, while retaining the advantages of the solution process for polymerization of olefins.

The linear polymers precipitated from the solutions obtained by the process of this invention are useful in many applications, especially in the form of films, molded and extruded articles, such as tubing, extruded insulation on wire, filaments, and impermeable coatings for paper.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process of producing polyolefins which comprises introducing an alpha-olefin, an inert non-polymerizable solvent therefor and for the polyolefin to be produced, and hydrogen into a reaction zone, the amount of hydrogen present in said zone being less than 60 parts per million by weight based on the total reactor feed, polymerizing said olefin in said reaction zone with a catalyst formed by admixing from one to two compounds of the class consisting of titanium salts, vanadium salts, titanium alkoxides and vanadium alkoxides with a compound having at least one metal-to-hydrocarbon bond, maintaining said reaction zone at a temperature such that the said polyolefin remains dissolved in said solvent, maintaining in said reaction zone an excess of said olefin in said solvent, and recovering said polyolefin from said solvent.

2. A process of producing polyolefins which comprises introducing an alpha-olefin, an inert non-polymerizable solvent therefor and for the polyolefin to be produced, and hydrogen into a reaction zone, the amount of hydrogen present in said zone being less than 60 parts per million by weight based on the total reactor feed, polymerizing said olefin in said reaction zone with a catalyst formed by admixing from one to two compounds of the class consisting of titanium salts, vanadium salts, titanium alkoxides and vanadium alkoxides with a compound having at least one metal-to-hydrocarbon bond, maintaining said reaction zone at a temperature above the melting point of said polyolefin, maintaining in said reaction zone an excess of said olefin in said solvent, and recovering said polyolefin from said solvent.

3. The process of Claim 1 in which said alpha-olefin is ethylene containing a minor amount of a second alpha-olefin, whereby a copolymer is produced.

4. The process of Claim 3 wherein said second alpha-olefin is 1-buten .

5. The process of Claim 1 wherein said inert solvent is cyclohexane.

6. The process of Claim 1 wherein said inert solvent is pentane.

7. The process of Claim 1 wherein the amount of hydrogen present in said reaction zone is from about 4 to about 60 parts per million by weight based on said olefin.

8. The process of Claim 1 wherein said catalyst is formed by admixing titanium tetrachloride, anadium oxychloride and aluminum triisobutyl.

9. The process of Claim 1 wherein said catalyst is formed by admixing titanium tetrachloride, vanadium oxychloride and aluminum triisoprenyl.